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Feature Article

Computer modeling of polymer crystallization – Toward computer-assisted materials' design

Takashi Yamamoto

Department of Physics and Informatics, Yamaguchi University, Yamaguchi 753-8512, Japan

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ABSTRACT

Crystalline polymers are very interesting and useful materials with great versatility through their potential morphology control. Recent surge in computer modeling studies has its origin both in increasing need for efficient methods of materials' design and in tremendous developments in computer power that is expected to meet the need. In this paper, we briefly survey the present state of computer modeling of polymer crystallization with the aim to foresee future developments. We first review simulations of crystallization in simple polymers under quiescent conditions where most of the efforts have hitherto been devoted. We also examine recent studies on crystallization under flow or large deformation. Then we present our ambitious plans to extend the simulation methods to polymers having complex chemical structures, though it is still an uncultivated field of research. We also refer to the new modeling strategies which integrate macroscopic and microscopic methods, and to the possibilities of molecular modeling in polymer nanotechnologies. Though our goal seems very far, there are obviously very fertile lands for the computer simulation studies.

1. Introduction

Many useful materials in the future are expected to be created with various self-organizing molecules. Self-organization of polymers has also been investigated intensively, and we can find many reports for example in a recent proceeding of Faraday Discussion "Self-Organizing Polymers" [1]. Crystallization is a typical case of polymer self-organization, which has long been investigated since the discovery of chain-folding as the principal mode of crystallization. The chain-folded lamellae are main building blocks of polymeric materials and their spatial distribution dominates all physicochemical properties of the materials. Crystal structures and crystallization mechanisms are therefore central subjects in science and technology of polymers.

Besides great industrial significance, polymer crystallization entails many peculiar problems of academic interest, the mysteries of self-organization in soft giant molecules driven by specific long-range interactions. Close relevance to various problems in molecular biology of DNAs and proteins is also anticipated. The long-standing but still controversial problems in polymer crystallization were best reviewed in the historical proceeding of Faraday Discussion in 1979 [2].

Many stereo-regular polymers, whether synthetic or biological, form partially crystalline solids, which consist of crystalline lamellae and intervening amorphous layers [3]. The crystalline polymers are known to show characteristic multi-scale structures ranging from local crystalline structure to macroscopic structure of spherulites (Fig. 1). The crystal structure of polymer is almost uniquely determined as the lowest free-energy state, and the energy analyses by computer modeling have contributed much to the structure determinations [4–6]. Thermal properties and phase transitions in polymer crystals have also been the subjects of innumerable simulations, and we can here cite just a few studies [7–16]. On the other hand, the large-scale structure, the way of lamellar stacking or branching for example, may be determined by the balance of equilibrium and kinetic processes of crystallization. They show a great deal of varieties depending on the crystallization conditions such as temperature, pressure, solvent as well as on molecular structure itself [3,17–19].

Polymer crystallization is very sluggish, especially near the melting temperature, and usually takes place with kinetic controlled mechanisms under thermodynamic conditions far from equilibrium. Molecular processes in such non-equilibrium conditions may only be rigorously followed by direct molecular level simulations, such as molecular dynamics (MD) or Monte Carlo (MC) methods. However, due to its extremely slow dynamics, polymer crystallization has long been far out of reach of the conventional molecular simulations [20–22]. In this review, we briefly survey the present state of computer modeling of polymer crystallization, and seek for future prospects of the modeling studies.

E-mail address: yamamoto@mms.sci.yamaguchi-u.ac.jp

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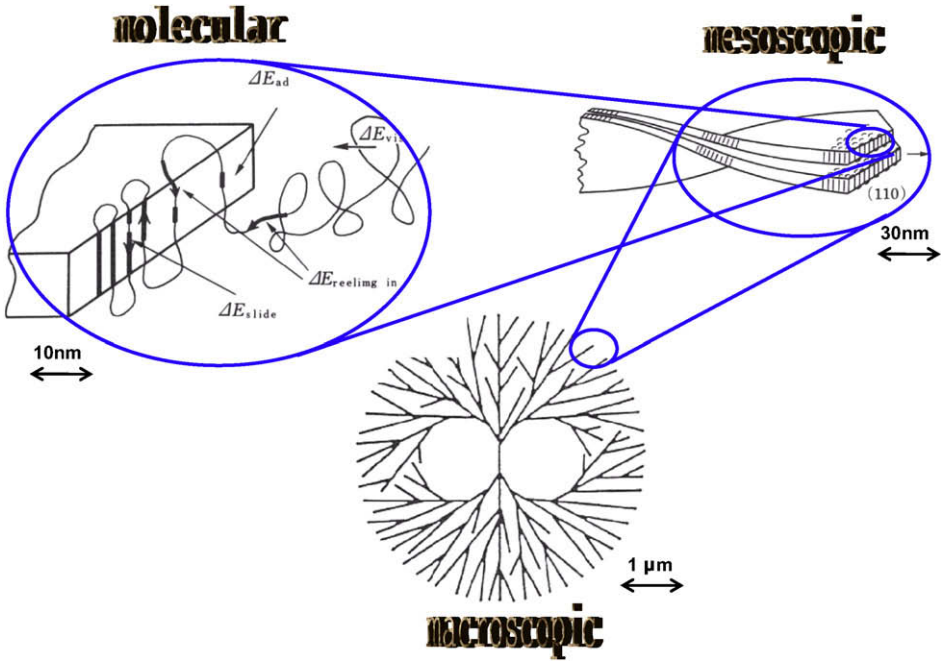

Fig. 1. Multi-scale structures of crystalline polymers, from molecular-level structure of the lamella crystal growing by reeling in random coiled chains in the melt, to mesoscopic-level structure of growing lamellae showing cooperative layering and twisting, and to final macroscopic spherulitic aggregate of the lamella.

2. Polymer crystallization

Crystallization of flexible polymers with a large number of internal degrees of freedom involves very complicated molecular motions of various space and time scales, ranging from large scale transport of whole chains to atomistic scale rearrangement of crystalline stems in perfecting crystalline order. In contrast to the global chain dynamics in the melt, the molecular motions during crystallization can be very sensitive to the chemical structure just like the crystal structure being specific to the structure of constituent molecules. Thanks to intensive work of nearly half a century, however, very universal macroscopic rules have been found for example in the temperature dependence of crystal growth rate and lamellar thickness. Their molecular level origins have long been the focuses of innumerable experimental and theoretical investigations.

On the basis of the secondary nucleation mechanism, a framework of the molecular scenario was first proposed by Lauritzen and Hoffman (LH) soon after the discovery of chain-folded crystallization [23]. Due to the great success of the LH-theory especially in predicting characteristic changes in lamellar thickness and crystal growth rate with crystallization temperature T_c, most of the discussions thereafter have been concentrated on understanding various experiments in terms of the LH-theory. As is often the case with the first order approximation, the LH-theory adopted bold simplifications about the elementary processes of chain deposition and folding, which have however raised various arguments to find out more natural molecular mechanisms and to resolve paradoxes inherent in the LH-theory [24].

As for the very beginning of crystallization in isotropic melt, the presence of unknown impurities in polymer samples has long obscured the primary nucleation mechanism, and we could find only limited number of reports. Recent surge of investigations on the very early stages of crystallization will have an origin in the proposal of peculiar instability in undercooled melt before the onset of crystallization, a spinodal-decomposition (SD) or phase-separation assisted nucleation scenario [25]. Though its validity is still a subject of considerable arguments, this proposal undoubtedly stimulated investigations of the pre-crystalline state, the importance of which will be more clearly appreciated when we think of crystallization under flow or large deformation.

Emerging also is the new enthusiasm about novel crystallization in strongly confined systems; very thin film [26], polymers in a cylindrical cavities or nanorods [27], or nanodomains in phase separated block-copolymers [28,29]. The presence of surface or interface will cause strong constraints on polymer conformations and enforce peculiar chain trajectories during crystallization.

The polymer crystallization thus involves quite new topics as well as historical unsolved problems. Long flexible polymers are considered to show chain-folded crystallization from highly entangled states by reeling in their chain tails. However, experimental knowledge available is mostly macroscopic, and detailed molecular processes of polymer crystallization are not readily accessible. It is the fundamental task of the theoretical work to find out possible molecular pathways from mechanical and statistical–mechanical points of view. However rigorous analytical treatments are very difficult for polymers with large internal degrees of freedom and specific long-range interactions, and we are inevitably led to computer simulations to tackle such formidable tasks.

In the following sections, we first review simulations of crystallization in simple polymers under quiescent condition where most of the efforts have hitherto been devoted. Then we survey a few recent studies on crystallization under flow or large deformation. Lastly we explain new efforts to explore vast uncultivated field of research on polymers with complex molecular structures, where our goal seems very far but there are obviously fertile lands for computer simulation studies.

3. Crystallization under quiescent conditions

Crystallization in polymers is usually divided into two separate processes, the emergence of small crystalline domains called primary nuclei, and their subsequent growth. The primary nuclei are nanometer-sized structures whose shapes may be treated by equilibrium thermodynamics, while the growing crystals have very thin platelet shape which must be kinetic controlled.

3.1. Emergence of the crystalline order

Since early 50s, innumerable simulation studies on polymer solution and melt have been reported. However, the first report on crystallization of chain molecules, as far as the author is aware, was for short *n*-alkanes by Roe et al. in 1988 [30]. They observed fast crystallization of alkane molecules into platelets. A limited number of studies have since followed, on crystallization and melting in alkanes of various chain lengths [31], on transient pre-crystalline state in undercooled melt [32], on steady-state growth of lamella [33], on crystallization in ultra-thin films [34,35], etc.

The primary nucleation in polymers did not attract much attention probably because of ubiquitous heterogeneous nucleation due to impurities. Conceptually the primary nuclei are imagined as either neat chain-folded crystallites or fringed micellar clusters depending on the way how the constituent chains participate in the nuclei formation [3]. But the direct approach to the problem by computer simulations must await a research in the mid 90s.

3.1.1. Primary nucleation from solutions

The memorial simulation for polymer nucleation was given by Kavassalis and Sundararajan (KS), who first demonstrated a clear transition in polyethylene (PE) from a globular state to a chain-folded crystallite, where the driving force for crystallization was dominantly van der Waals attraction between constituent atoms [36]. The resulting chain-folded crystallite was rod shaped along the chain axis direction; the conformation will be near the energy ground-state judging from the expected large fold-surface energy compared with that of side-surface (Fig. 2). They considered a single chain in a vacuum, where all possible effects of solvent molecules were ignored. In addition, their PE model adopted was much stiffer than real PE molecules, while it is now well appreciated that crystallization rate is sensitive to the chain stiffness [37,38]; indeed realistic PE model was shown to crystallize more slowly [39]. Despite these limitations of the KS model, the first demonstration of the chain-folded crystallization was very encouraging. Indeed there followed many studies, by adopting similar models and methods, on detailed pathways of PE crystallization [40], and crystallization in PE of various topologies [41–43].

To consider solvent molecules explicitly is not an easy task computationally. An approximation is to take only solvent viscosity into account by using Brownian-dynamics (BD) or Langevin-dynamics (LD) method. Muthukumar et al. considered crystallization of a single chain by the LD-method assuming moderate degree of viscous damping [44]. The presence of solvent friction did not change the final rod-like form of the nucleus, but seemed to hinder rapid collapsing into globules. Especially marked was the longer chain; it first formed local crystalline regions they called "baby nuclei", which then gradually coalesced and formed a large chain-folded crystal (Fig. 3). Similar local clusters linked by connecting segments were also noticed in usual collapse transitions in three-dimension (3D) [45], and also in 2D crystallization of strongly adsorbed chain on crystal surface where motions of the chains were partially hindered by the local adsorption onto the surface [46].

For such small systems of a single chain, the final 3D form of the cluster will be determined as the lowest free-energy conformation with minimal kinetic arrest. The free-energy landscape for the crystallizing PE chain was estimated by the histogram method at given crystallization temperature T_c [47]. Discrete states well separated in their radius of gyration or lamella thickness corresponding to different integer-fold conformations were found to have local free-energy minima (Fig. 4). Though the free-energy landscape for longer chains will become increasingly steeper and rugged with consequent larger probability of being trapped at local equilibrium conformations, the presence of minimum free-energy conformations and their changes with temperature were also verified [48]. In simple liquids the primary nuclei are considered to emerge through equilibrium fluctuations [49]. The conclusion about the chain-folded nucleus of PE is in agreement with the general picture of critical nuclei for small molecules. Unfortunately, full-atomistic simulations taking solvent molecules into consideration are very few. A recent study by Fujiwara considering PE crystallization in *n*-hexane solution showed slightly different crystallization from that in vacuum, but many problems remain to be studied [50].

3.1.2. Primary nucleation from the melt

With ever increasing computer performance, simulations in much larger systems have become feasible. However, full-atomistic approaches to polymer crystallization need extremely large computer power even in the case of simple polymers, and appropriate modeling or coarse-graining of the system is imperative. From a series of work on the development of coarse-grained models for polymers, Mayer and Muller-Plathe have build up a model of poly(vinyl alcohol) (PVA) for studying early stage of crystallization. They investigated the emergence of crystalline order from the isotropic melt by rapid quenching [51,52]. They could reproduce many elementary processes of homogenous nucleation that showed good correspondence with experiments and other simulations, in temperature dependence of lamella

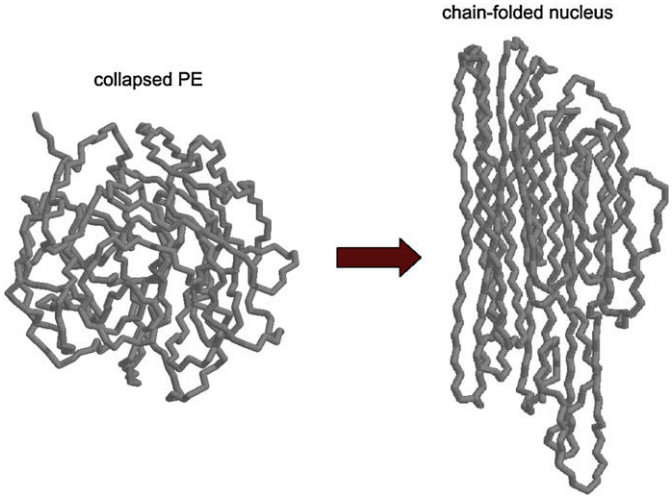

Fig. 2. Formation of a crystal nucleus of a single PE chain in a vacuum. The chain conformation changes from a spherical globule to a stretched rod.

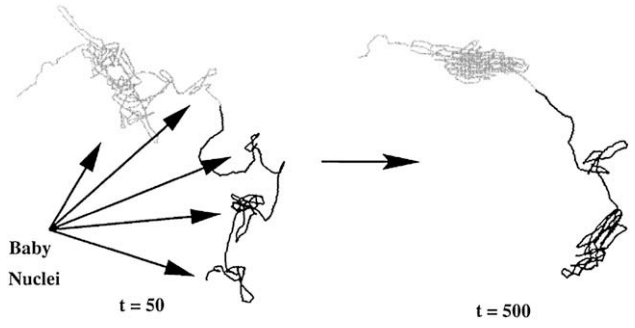

Fig. 3. Formation of baby nuclei during crystallization of a long PE chain of 2000 CH_2. Initial baby nuclei gradually coalesce and finally form a large single cluster (from Ref. [57]).

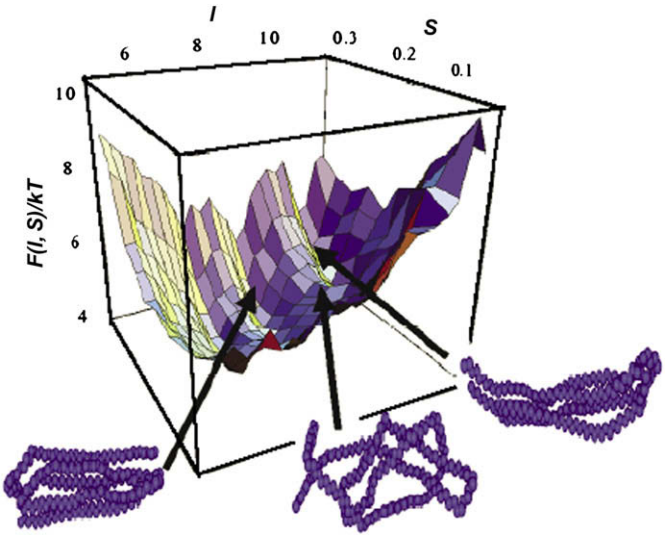

Fig. 4. Energy landscape of a short PE chain during collapse and crystallization. The free energy is plotted vs. order parameters, radius of gyration along the chain axis (l) and the orientational order parameter (S); shown also are two local minimum conformations and the transient state at the saddle energy point (from Ref. [47]).

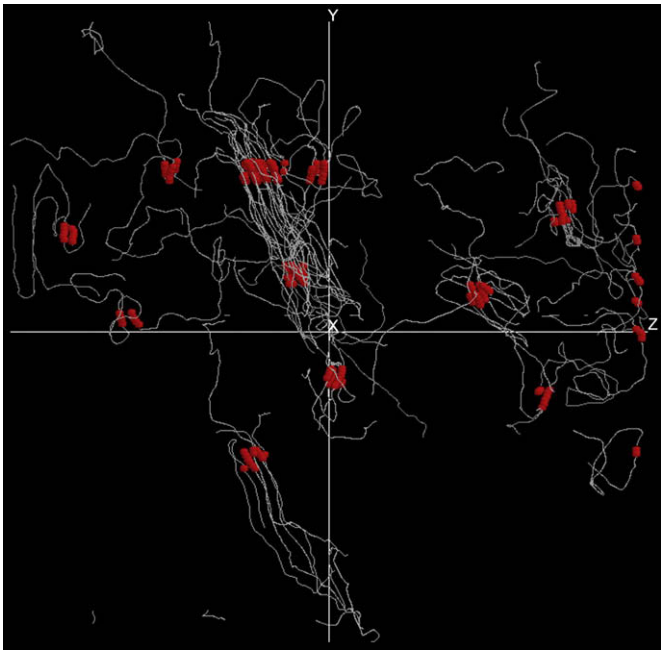

Fig. 5. Chain conformations of the primary nuclei for model PE in crystallization from the melt; only chains composing the nuclei are depicted; the chain segments painted in red are those having higher crystalline order. If we consider the red regions as purely crystalline nuclei, the chains seem to have the fringed micelle-like structures, but overall chain conformations look like the chain-folded nuclei markedly elongated along the chain axis directions.

thickness, structure of fold surface, etc. In their work, they neglected long-range force (van der Waals attraction) to accelerate computation. Their model has the energy contribution due to intrachain interactions only and the dominant driving force for crystallization is entropic, which seems to ignore dominant driving force for polymer crystallization in conventional sense. However, their work is reminiscent of the classical solid–liquid transition in systems of repulsive spherical atoms [53] and poses an intriguing problem as to the intrinsic driving force for polymer crystallization.

Usual image of initial crystallization in the melt is a primary nucleation. The structure of the primary nuclei in the melt should be compared with those in solution described before. In the case of melt crystallization two distinct images of the primary nucleus, chain-folded nucleus and fringed micelle nucleus, have long been conceived. Molecular simulations must give definitive answer to this question. We have adopted a PE-like molecular model and investigated homogeneous nucleation from highly supercooled melt [54]. By first identifying the primary nuclei and thereby examining individual conformation of the chains forming the nuclei, we found that the primary nucleus in the melt has similar elongated rod-like structures as those observed in vacuum or in solution (Fig. 5). The overall shapes of the nuclei in the melt are, however, highly perturbed, and the interfaces between the nuclei and the surrounding melt are not so definite [54].

Rigorous MD approaches to the structure of highly undercooled melt were attempted by Gee et al. using rather realistic models of PE and poly(vinylidene fluoride) (PVDF), though the molecular models were again slightly modified to facilitate crystallization [55,56]. Systems of millions of atoms were considered to investigate mesoscopic-scale density fluctuation proposed in the SD scenario. From these simulations, they obtained affirmative results showing peculiar density anomaly at the very early stage of crystallization, and they concluded that this is really an indication of the SD mechanism. However, real space image of the simulated density fluctuation and its molecular origin are not well documented. As to the density anomaly in the supercooled melt, Meyer et al. made contrary observation that there is no density fluctuation having specific wave length [52]. Muthukumar et al. [57] also made a critical discussion on the basis of their LD simulation for a single chain and dynamical structure factor $S(q,t)$ which has shown apparent resemblance to that considered as the evidence of SD mechanism [25]. They argued that the characteristic SAXS peak may not be an indication of the SD mechanism but simply due to the interference between baby nuclei of small crystalline clusters [57]. Emergence of local crystalline order in highly-quenched melt, whether it is due to usual primary nucleation or phase separations, may depend sensitively on molecular properties such as chain rigidity or chain length. Further investigations are obviously needed to clarify the confusion.

3.2. Growth of the chain-folded lamellae

Polymer lamellae show steady growth through chain-folded crystallization irrespective of the type of initial nucleation, homogeneous or heterogeneous, to form various higher order structures. The crystal growth has been the central issue in the study of polymer crystallization, since the final morphology of polymer solid is dominated by the growth process of lamellae. Contrary to the homogenous nucleation discussed so far, basic molecular processes of the crystal growth are those that take place at crystal–solution or crystal–melt interface, the crystal growth front, on which the molecules diffuse, adsorb, and crystallize (Fig. 6). The standard LH-theory of polymer crystal growth has succeeded in explaining various observations. But the theory is phenomenological one based on many assumptions on the molecular pathway and the microscopic structure of growth surface, for which various criticisms have been directed. Many independent molecular scenarios have been put forward, such as modified surface nucleation models by Point [58], Keller [59], Hikosaka [60], rough surface growth model by Sadler [61], molecular nucleation theory by Wunderlich [3], bundle nucleation model by Allegra [62], or mesophase-domain mediated growth by Strobl [63]. In every effort to verify the assumed scenario, however, we were taught that real molecular trajectories of crystallizing chains at the interface are too

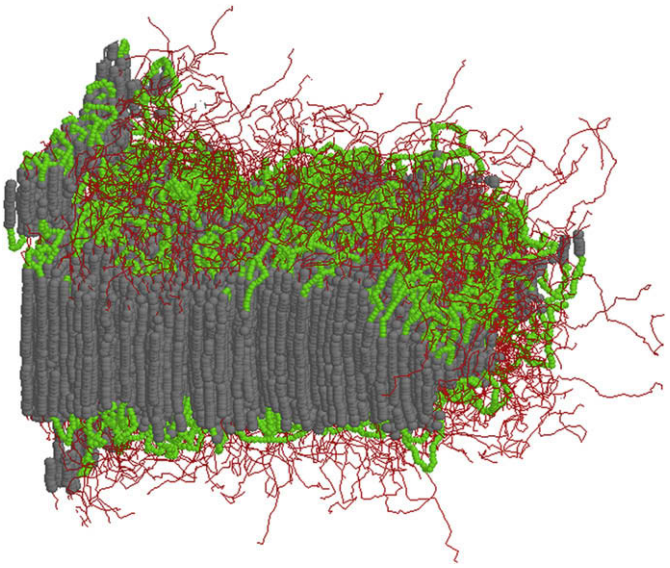

Fig. 6. Chain-folded lamella growing in the melt from the left crystal substrate; the figure was generated by our MD simulation for 1280 chains of PE-like molecules (Ref. [54]). Segments are depicted according to their types, crystalline stems in dark gray, folds in green, and cilia in red.

hard to seize by experiments. The molecular simulation that enables to "see" individual molecules must provide a unique tool to reveal molecular pathways of crystallizing chains.

3.2.1. Crystal growth from solutions or vacuum

Computer simulation of crystal growth in polymers has also begun with a very simple system. Early studies were concentrated on the dynamics of a single chain strongly adsorbed on a flat growth surface and undergoing collapsing and chain-folded crystallization [46,64]. These were the first attempts to observe molecular processes of secondary nucleation on the growth front. An initial random coil chain first showed local collapse to form two-dimensional necklace of crystallites, similar to the "baby nucleus" described by Muthukumar in solution crystallization (Fig. 7). Then the global reorganization into larger 2D lamellar crystal followed through coalescence of the crystallites. Such two stage process is a natural consequence of the slower global collapse than local clustering, which is expected in longer chains at larger supercooling or in chains whose motions are temporally arrested by local adsorption onto the substrate. The resulting 2D lamellae were found to be regularly chain-folded and to have larger thickness at higher crystallization temperatures in good agreement with experiments [46,64]. In addition we found that the very embryonic states were not single extended stems as conceived by the LH-theory but hairpins of a pair of stems [46], the observation of which is consistent with the detailed calculation of the free-energy during secondary nucleation by Doye et al., where the release of constraints on the kinetic path was found to eliminate the free-energy barrier located at the first-stem deposition step [65]. It was also found that the 2D lamella formed at T_c shows pronounced thickening when heated above T_c, where the whole crystalline chain shows highly cooperative sliding motions along its contour [46]. The basic assumption of strongly adsorbed chain in these simulations might seem unrealistic as a model of solution crystallization. However, Doye et al. have also shown a phase diagram of the crystallizing chain, in which a 3D random coil first transforms into a 2D random coil being adsorbed on the crystal surface, and then it crystallizes by further lowering the temperature [65].

The next step that should be taken was to extend the 2D model to 3D, where both chain diffusion toward and chain adsorption followed by crystallization on the growth front must be considered. In crystal growth from solution, as in the primary nucleation, explicit consideration of solvent molecules would make simulations very time consuming. The polymer chains were therefore assumed to be in vacuum or in poor solvents. We considered a long PE-like chain placed near the (100) surface of the hexagonal lattice and studied adsorption and crystallization of the chain [66]. Due to strong attraction to the surface, the chain quickly adhered to the surface and formed a droplet. At high T_c larger molecular mobility or lower droplet surface tension made it spread quickly over the surface, while at lower T_c the droplet tends to form hemispherical conglomerate. From such strongly adsorbed state, the chain-folded crystallite developed, where chain entanglements in the initial droplet were pushed away from the crystalline region into the

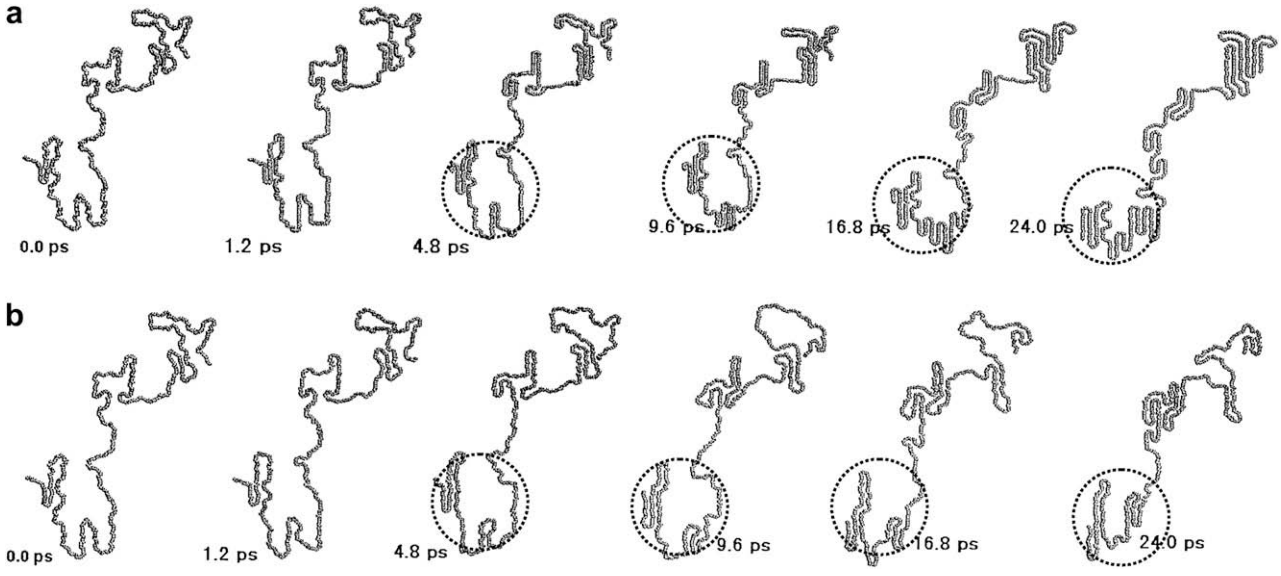

Fig. 7. Snapshots of a chain crystallizing on the crystal substrate by rapid quenching to (a) 50 K and (b) 300 K. Appearance of local clusters of paralleled stems, mostly paired, is noticed. Average stem length is longer at higher crystallization temperatures.

amorphous (Fig. 8). Muthukumar et al. also made LD simulations of adsorption of multiple chains [44]. Though the presence of solvent molecules was implicit in their simulation, strong interchain interactions between polymers caused formation of clusters which subsequently adsorbed to the substrate. In real crystallization from solution, it is not always clear whether the crystallizing polymers are collapsed like those in poor solvents or more extended. Detailed molecular trajectories of the crystallizing chains may depend crucially on the initial conformation of the adsorbed chains.

3.2.2. Crystal growth from the melt

Crystallization from the melt would be most frequently met in polymers. In comparison with crystallization from solutions, melt crystallization does not need long-range diffusion of chains because of sufficient chain supply. Except restrictions on the chain mobility due to larger viscosity or chain entanglements, crystallization from the melt is expected to be faster than that from dilute solutions. However, even in the most favorable case of PE, usual growth rate of lamellae is desperately slow. For example the maximum growth rate is about 10^{-4} nm/ns for PE of $M = 10^5$, and therefore very realistic modeling would be beyond execution by present day computers [67]; acceleration of crystallization by adopting proper polymer model is indispensable in studying crystal growth in large systems.

We adopted a simplified polymer model of PE, where the chains were made of CH_2 united atoms but the equilibrium bond angles were assumed to be 180°. By properly adjusting chain flexibility, however, physical properties of PE relevant to crystallization, such as melting point, heat of fusion, and diffusion coefficient of the chains, were found to be reproduced [68,69,54]. We made MD simulations for a large system of 1280 chains of relatively short PE C_{100}, and succeeded in observing steady-state growth of chain-folded lamellae from the melt at various T_c (Fig. 9) We found that each molecule participating in the chain-folded crystallization shows multistep processes of local adsorption of short stems followed by stretching of the stems to the crystal thickness, finally giving rise to nearly integer-fold lamellae but with marked taper-shaped growth fronts. Since all the atomic-scale data for the chains are at hand, we can calculate various dynamic and static structures of the system. For example, we found that the structure of fold surface generated through rapid kinetic process corresponds well to that predicted from equilibrium considerations [70,71], and that the growth front shows large kinetic roughening at larger undercooling [54]. We also found that the structure of the supercooled melt exhibits no anomaly at least around the usual temperature region where the steady-state growth of lamellae is observed without occurrence of homogeneous nucleation.

At the end of this section, we must comment on important contributions by MC approaches. Based on the phenomenological models of LH and Sadler–Gilmer (SG) but with partial release of assumptions originally introduced for ease of analytical treatments, detailed molecular pathways of crystallizing polymers were reconstructed by use of kinetic MC method. Though assumptions inherent in the LH and SG models still remain, the method was free from slow dynamics of chains and was able to give new insights overlooked in the original versions of the theories [72]. Other MC approaches closer to molecular simulations described so far are the lattice MC simulations of polymer crystallization. Since the early work by Flory, lattice models have provided simple frameworks to understand polymer phase transitions [73]. With recourse to efficient models and MC moves, such as the bond fluctuation model with global moves, the crystal growth in model polymer systems was studied [74,75]. Though the approaches seem to have intrinsic limitations as to the reality of chain motions and the fidelity in chemical structures, they have a great merit of allowing fast simulation. The MD and MC methods are considered to give compensatory information about polymer crystallization.

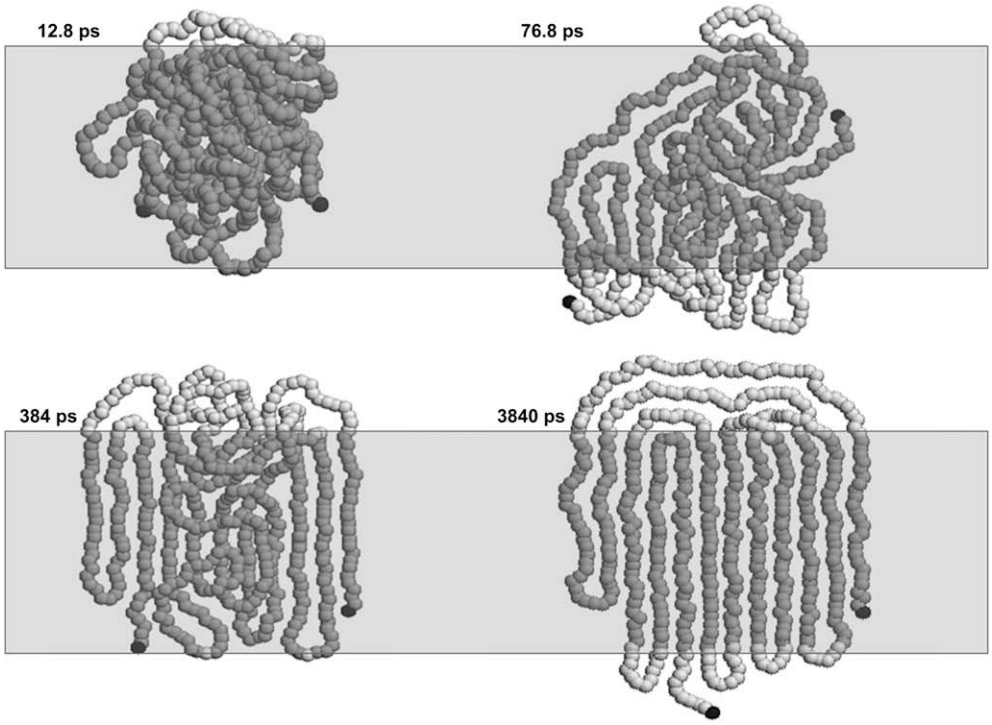

Fig. 8. A long flexible PE-like chain adsorbing and crystallizing on the lamella-surface (shaded); atoms sited upon the crystal surface are painted in dark gray, while those in the amorphous regions outside the crystal surface are painted in light gray. We can notice that initial chain entanglements are gradually pushed away into the amorphous regions.

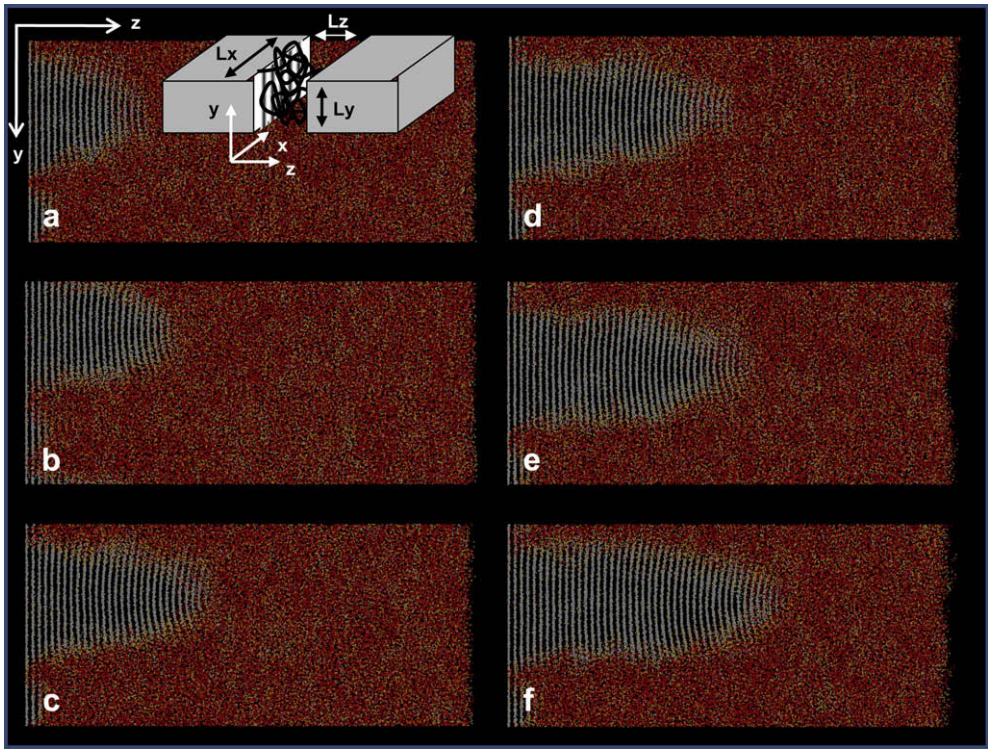

Fig. 9. Crystal growth of relatively short PE-like chain in the melt which was placed between two crystal substrates (inset). Pictures show growing lamellae viewed along the *x*-axis, where the chain axis is along the *y*-axis; the parallel white lines show crystalline stems; (a) at 28.8 ns, (b) 38.4 ns, (c) 48.0 ns, (d) 57.6 ns, (e) 67.2 ns, and (f) 76.8 ns. The lamellae are making steady-state growth from the left substrate into the melt region (red) and have pronounced taped edge at the growth front.

4. Crystallization under flow or large deformations

In most industrial processing of polymers, such as fiber or film formation, crystallization takes place under flow or large deformation, where molecular mechanisms quite different from those in quiescent states would be working. Polymers have very long relaxation time, within which specific melt structure is maintained and crystallization therefrom gives characteristic textures.

Chain orientation in the pre-crystalline melt causes lower entropy of melting, thereby increasing thermal stability of the crystal at higher temperatures. It is very likely that the increase in melting point gives larger effective supercooling and faster crystallization. However, the time-dependent structure of initial oriented melt and the way crystalline order develops are quite obscure. In spite of great academic and industrial significance, corresponding molecular simulations of crystallization are quite few. In this section we review some recent investigations.

4.1. Crystallization from flowing solutions

Elongational or shear flow in polymer solution stretches the chains, preferentially longer chains, and causes the emergence of core fiber (shish) over which usual chain-folded lamellae (kebabs) grow. As far as the present author is aware, no rigorous simulations taking flowing solvent molecules into consideration are yet reported. By describing the solvent flow by simple mean-field for polymer chains, Muthukumar et al. investigated crystallization of polymers in elongational flow [76]. Above a critical flow rate, the chains showed a bistable transition from the coiled to the stretched conformations, and the stretched chains formed a shish-like structure; large hysteresis observed in the transition addressed a question about the conventional picture that longer chains dominantly form the shish. While coiled chains around the shish gave rise to the kebab formation, the propensity for the kebab was found larger under lower flow rate and/or larger crystallization rate.

Development of a kebab-like structure was also observed around an attractive rod in quiescent condition. Hu et al. considered a rigid rod, actually a single extended chain, as the shish and observed the growth of regularly chain-folded lamellae of constant thickness around the rod by use of a lattice MC calculation [77]. In this work, the chains were simply precipitating around the central rod and the flow-field had nothing to do with the formation of the kebab.

4.2. Crystallization from oriented melt

Full-atomistic modeling of fiber formation would be more tractable in deformed melt than in flowing solution, since the pre-aligned amorphous chains are expected to crystallize much faster. Koyama et al. studied crystallization of long realistic model of PE from its oriented amorphous state [78,79]. They first prepared highly oriented amorphous sample by cold-drawing of an isotropic amorphous state, and then they heated the sample to various crystallization temperatures. They clearly observed the emergence of highly oriented crystals, of hexagonal chain packing due to the united atom model adopted, within several tens of nanoseconds (Fig. 10). Probably due to rapid crystallization and limited system size, primary nucleation and crystal growth could not be separated, but the overall crystallization rate vs. temperature showed a typical bell-shape with a maximum around 330 K. Development of various parameters, such as mass density, van der Waals energy, fraction of *trans* bonds, average *trans* segment length, etc., showed quite universal time dependence during crystallization, which is a clear indication of a single mode of crystallization.

Independent investigations of crystallization in orientated PE were carried out by Rutledge et al. under various deformation conditions [39,80]. They found that active deformation promotes

chain extension and orientation but not crystal nucleation, while relaxation of stress at constant strain gives chain reorganization and rapid nucleation and growth. They also studied crystallization vs. temperature and found marked lamella thickening as well, and confirmed the temperature dependence of the lamella thickness in good accord with experiments.

The systems considered so far are still very small with strong effects of periodic boundary conditions being suspected, and the melt structure prior to crystallization may not be realistic enough. Indeed, the shish–kebab formation was not observed. However, these works will be a springboard for future resolution of long-standing arguments on fiber formation.

5. Crystallization in helical polymers

Great efforts over several decades have revealed universal macroscopic rules in polymer crystallization and have contributed to establishing molecular theory of polymer crystallization. Many polymers, even though they have complex chemical structures, are considered to follow the same universal rules of polymer crystallization. However, when we look at the polymer crystallization in different angles or magnifications, it can be very specific, just like the crystal structure is, in absolute rate of crystallization, in final crystallinity attained, in detailed way molecules fold on the growth surfaces, etc. Molecular theories of polymer crystallization available are only for limited macroscopic properties such as the dependence of growth rate or lamella thickness on temperature, where molecular characteristics are renormalized in a small number of parameters such as heat of fusion, surface free energies, and molecular diffusivity.

Simulation studies described so far were all concerned with simple straight polymers such as PE, and the basic interest there was mostly in the trajectories of crystallizing chains regarded as structureless strings. When we go further into details of individual polymers having complex chemical structures, there appear other problems. Many polymers, either synthetic or biological, have helical conformations. Great endeavors have been made to elucidate coil–helix or coil–globule transitions in single helical polymers [81]. Crystallization we are interested here is a many-chain problem where intramolecular and intermolecular degrees of freedom cooperate. The chain conformation of isotactic poly(propylene) (iPP), for example, has no a priori chirality; it takes either R- or L-handed helical conformation in the crystal with equal probability, but each crystalline stem selects one of the two chiral conformations by crystallization. Furthermore, the crystalline order enforces additional symmetry that the crystal must take either the chiral β-form of one handed helixes or the achiral α-form of alternating R- and L-handed helixes. In the molecular process of chirality selection, the crystalline stems must efficiently recognize their helical sense in order to build up proper crystalline order.

Encouraged by the success in simple polymers, some attempts have been made to simulate crystallization in iPP, but it was found too slow to be observed by realistic simulations [82,83]; even a coarse-grained lattice model only yielded local ordering which is far from crystalline order attained in simple polymers [84–86]. We must find out narrow paths, with steep free-energy barriers both in enthalpy and in entropy, leading to the crystalline order in helical polymers.

There will be several possible origins of slow crystallization in helical polymers. We took up following two points in order to develop our computational catalyst. One is the intramolecular origin that large activation energy is needed in sweeping away helix-reversal defects to form ordered chiral conformations either L- or R-handed helix. Larger kinetic flexibility with frequent barrier crossing between the R- and L-handed conformations will make intramolecular ordering faster, while large equilibrium flexibility is known to disturb crystallization [38]. The other is the intermolecular origin. Large and complex steric collisions between constituent atomic groups will make favorable modes of chain packing less likely; they make the density of states for the favorable chain packing smaller and give rise to larger entropic barriers in accomplishing good chain packing. In addition, polymers having large side groups will have higher energy barrier for necessary disentanglement of chains during crystallization. Taking these things into consideration, we studied two extreme cases: bare helix of slim chain-backbone, and general helix having large pendant groups, iPP as an example [87–89].

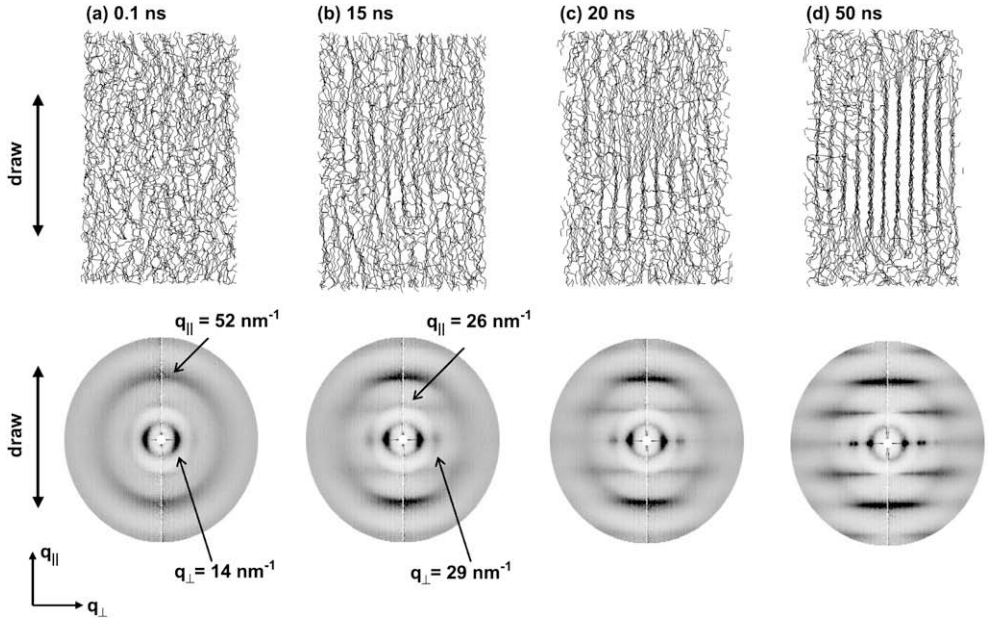

Fig. 10. Crystallization at 330 K from highly oriented amorphous state of PE. The initial oriented amorphous sample quickly transforms into crystalline fiber, with accompanying microscopic structural changes clearly demonstrated in the calculated structure factor $S(q_{\perp}, q_{||})$ given below.

5.1. Crystallization of bare helix

We here consider helical polymers essentially composed of backbone atoms only, such as poly(tetrafluoroethylene) (PTFE) or poly(oxymethylene) (POM). Helical conformations with long fiber periods, such as 13/6 and 9/5 for PTFE and POM respectively, give molecular contours of higher rotational symmetry around the chain axis, and the bare helix with nearly cylindrical molecular contour will make intermolecular steric repulsions very small. We considered the chain rather rigid having deep torsion potential minimum around the *gauche* positions giving approximately 4/1 or actually 9/5 helix just like POM, but with smaller torsion energy barrier against helix reversals. By gradual cooling similar to the process adopted in simple linear polymers, the single bare helix was found to transform rapidly from a random coil to a chain-folded conformation (Fig. 11) [88]. Though the rapid crystallization caused many helix-reversal defects to remain within the crystallite, they were gradually swept out of the crystalline region by long annealing at higher temperatures. Due to small steric collisions between adjacent helical stems, the chirality selection during crystallization was not conspicuous; the R- and L-handed stems seemed to be arranged at random within the crystal. The low chiral selectivity and consequent low entropy barrier in stem deposition process may give such fast crystallization.

The low chiral selectivity will be somewhat improved by assuming stronger interatomic interactions. However, stronger attractions would interfere with intramolecular ordering leading to a globular collapsed conformation [81]. Therefore we studied crystallization in short oligomers with stronger interchain interactions, and succeeded in observing the development of chiral domains composed of either the L- or the R-handed chains [89].

5.2. Crystallization of iPP

Crystallization in realistic iPP models was much slower. Even very gradual cooling of a single random coiled did not produce crystalline order but gave a random coil having short 3/1 helical segments only, which was quite in contrast to the bare helix. Local chain conformations at the helix-reversal defects are more complicated than those in the bare helix, and the intermolecular requirements in making crystalline packing are more complex giving higher entropy barriers.

Confinement of the crystallizing polymer to a low dimensional space will decrease the number of crystallization search paths and will lower the expected entropy barriers, besides eliminating chain entanglements inherent in 3D melt. Fig. 12 shows a typical chain trajectory reproduced for iPP in a narrow slit, where the chain was placed adjacent to the crystalline substrate (blue straight chain) made of perfect L-handed helix; this can be a simple 2D model for the crystal growth [88]. The random coiled chain of iPP showed pronounced ordering with decreasing temperature. Quite striking was the strict selection of the helical sense just opposite to that of the substrate helix. It was also found that if the helix deposits in a wrong sense, it rapidly reorganize into the right sensed helix through the propagation of the helix-reversal defects along the stem [90]. For the moment, crystallization with clear chirality

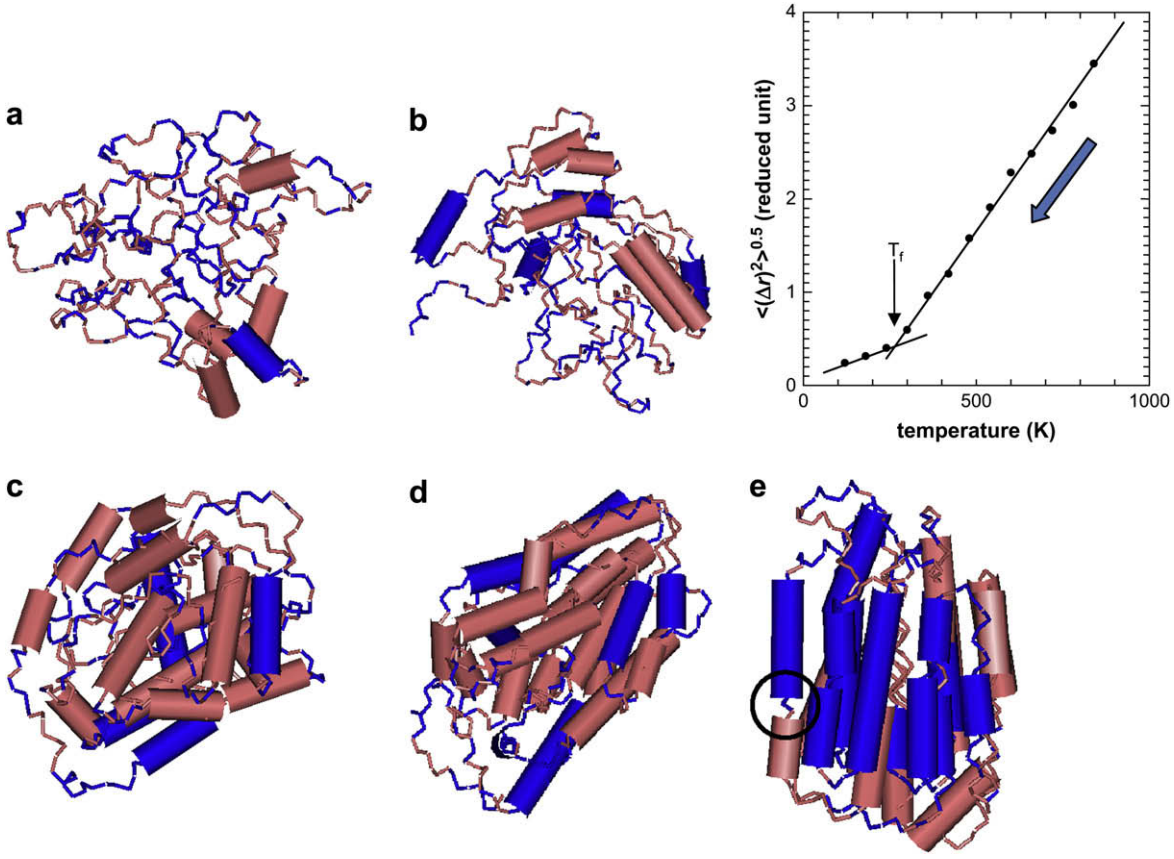

Fig. 11. Trajectory of the bare 4/1 helix of 500 atoms during stepwise cooling from 840 K down to 120 K. The helical segments, the sequences of *gauche*$^+$ or *gauche*$^-$ bonds longer than six bonds, are depicted by cylinders; right- and left-handed ones in different colors; at (a) 540 K, (b) 420 K, (c) 300 K, (d) 180 K, and (e) after 200 ns annealing at 300 K. Also shown is the average displacement of constituent atoms within 8 ps, the degree of dynamic deformation of the chain; an apparent freezing of chain motions is observed around 300 K.

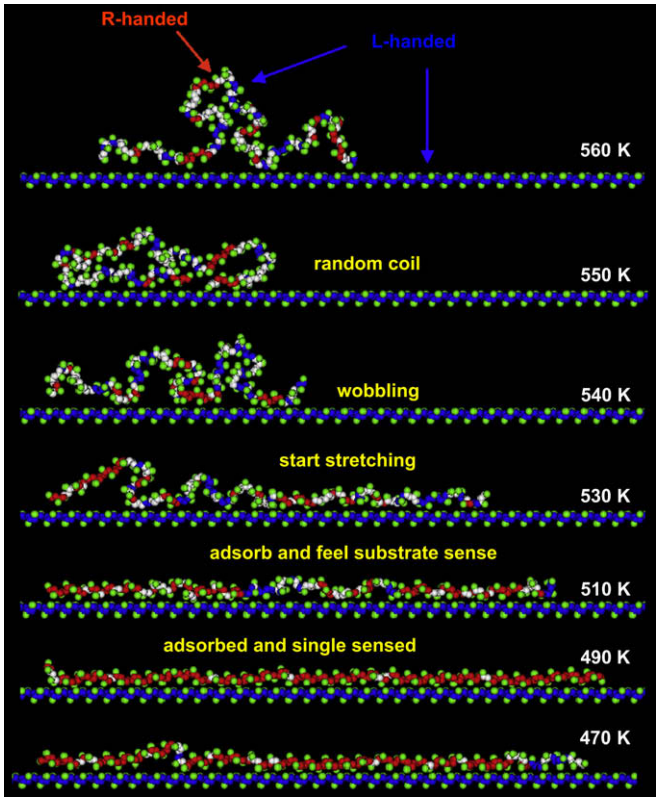

Fig. 12. An iPP molecule confined within a slit shows characteristic crystallization, with decreasing temperature, onto the substrate of left-handed iPP. During the stepwise cooling, 10 K/1 ns, the crystallizing iPP molecule shows strict chirality selection to take just the opposite helical sense to that of the substrate helix.

selection was only observed in very limited cases. However, it was strongly suggested that such molecular mechanism is operative at the 3D growth front of real iPP crystals.

6. Problems and challenges of future computer modeling

6.1. Theory of polymer crystallization

The molecular simulation of polymer crystallization has started only for these ten years, and many of the problems described in this paper remain unsolved. The simulation has just come up to the level that can reproduce mesoscopic scale crystallization in simple polymers. From the data accumulated so far, we must extract essential features of polymer crystallization to construct consistent molecular scenario. A big challenge remaining is a simulation of much longer chains at lower supercooling; molecular simulations are now still limited for relatively short chains and/or at extremely undercooled state. Also deficient are rigorous treatments of solution crystallization taking explicit solvent molecules into account, where roles of solvent molecules and possible salvation structures around the polymer molecules are expected to create a new chapter in polymer crystallization.

6.2. Crystallization of helical polymers

Helical polymers pose very interesting problems, about which we only described rudimentary works. Many interesting features of crystallization in helical polymers are expected to be revealed, chirality selection during crystallization as an example. Development of effective simulation methods is indispensable for further exploration into self-organization of polymers of much more complex chemical structures. However, simulation approaches to the crystallization in helical polymers involve similar difficulties as those well known in protein structure studies. Efficient use of MC methods or combination of MC and MD methods together with judicious choice of the lattice and the off-lattice approaches would be very important.

6.3. Formation of macroscopic structures

Crystalline polymers exhibit multi-scale structures (Fig. 1). As described so far, extensive efforts have been made to reveal molecular mechanisms of polymer crystallization, and MD and MC simulations have now come to reach the scale of several tens of nanometers. For further scale-up of the modeling to macroscopic structures a slightly different approach, besides standard mesoscopic modeling methods of much interest these days [91], would profit where one considers larger units as building blocks of the bulk polymer materials.

Muthukumar et al. have attempted to model macroscopic lamella growth via cluster aggregation process, through which they have shown both kinetic and thermal roughening of the lamella [92]; similar lines of studies taking finer building blocks, the rigid crystalline stems, were already reported to study the surface structures of *n*-alkane and PE [93]. Purely geometrical modeling of spherulites has also been reported recently, where the aggregation of stacked lamellae was investigated by proper space-filling algorithms, and the model spherulites obtained were utilized to study light scattering from and small molecule diffusion through the bulk crystalline polymers [94–96].

6.4. Polymer crystallization in nanospace

Crystallization in nano-composites or nanospace is an emerging topic of considerable interest. Several experiments and simulations of PE crystallization in composites with carbon nanotubes [97,98] and of crystallization in microphase separated domains of droplets [28,29,99] or nanorods [27,100,101] were reported. Also of great scientific and practical interest is the crystallization in very thin films [26,102]. Due to their limited number of atoms, nano-scale systems are especially suited for molecular simulations. Large effects of surfaces or interfaces, and competitions between characteristic length scales of lamella crystal and confining space are expected to give rise to distinct crystallization, and these are very challenging topics of molecular simulations.

7. Summary and conclusions

From the mid 90s, computer simulation studies of polymer crystallization have rapidly grown in number, expanded in space-time scales and in variety of problems treated. We have given a brief survey of the present status of the modeling studies mostly of molecular scales. The main interest there was in understanding basic elementary processes in polymer crystallization; the primary nucleation, the growth of the chain-folded lamellae, and the mechanisms of fiber formation. The targeted systems of the simulations have changed greatly from very small models of purely academic interest to rather large systems of several tens of nanometers that can match in size real polymer systems studied in polymer nanotechnologies.

Still remaining are problems to extend the simulation to polymers having more complex chemical structures. Though our journey to making it sufficiently useful and reliable tool may be long, it is undoubtedly very challenging task.

Development of macroscopic modeling methodology, which may be quite distinct from those of molecular level, is also very promising. To establish useful computational tool for materials' design in crystalline polymers, clever combination of microscopic and macroscopic schemes must be very important.

Computer modeling of self-organization in crystalline polymers is still young and uncultivated area of research. Besides contributions to the design of conventional polymer materials, the computer simulation method for crystalline polymers must have great potential in various molecular level designs of functional materials, such as polymer solar cells [103] or polymer batteries [104,13], for example. Computer modeling in crystalline polymers is only just beginning.

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Takashi Yamamoto is a Professor of Physics and Informatics at Yamaguchi University. He received his Ph.D. from Kyoto University in 1979 for his X-ray diffraction studies of high pressure phase of polyethylene. From 1985 he spent two years at Professor Strobl's Laboratory of University of Freiburg in Germany as an Alexander von Humboldt Research Fellow. His research subjects of interest are experimental and simulation studies of polymer crystals and crystallization, and he received the Award of the Society of Polymer Science Japan (2004) for his contributions to the computer simulation of dynamical structures of crystalline polymers and polymer crystallization.